- 1 -

OXYGEN SCAVENGERS INDEPENDENT OF TRANSITION METAL CATALYSTS

This invention relates to compositions for reducing the oxygen concentration present in an atmosphere or liquid (often referred to as oxygen scavenging). In one
5   particular application, the compositions are used in or in association with food packaging.

A wide variety of foods and other materials are susceptible to loss in quality during storage under atmospheric levels of oxygen. The damage can arise from
10   chemical oxidation of the product, from microbial growth, and from attack by vermin - much of which may be avoided by reducing the oxygen availability in the environment of the materials. In the field of packaging, relatively low-oxygen atmospheres have traditionally been generated
15   by vacuum packing and inert gas flushing. Such methods are not, however, generally applicable for various reasons. For example:

        - soft porous foods such as cakes cannot be subjected to strong vacuum;
20   - fast filling speeds generally preclude substantial evacuation of or thorough inert gas flushing of food packages;

        - filling some gas-flushed containers, such as be r bottles often results in occlusion of air;
25   - evacuation or flushing offers no residual capacity for removal of oxygen, which may have desorbed from the food or entered the package by leakage or permeation.

As a consequence there has been much interest in chemical techniques for generating low-oxygen atmospheres
30   and deoxygenating liquid or semi-liquid foods. Thus, there are approaches based on the use of oxidisable solids, for example porous sachets containing iron powder. In another technique, oxidisable MXD-6 Nylon is blended with polyester in the walls of blow-moulded
35   containers - the effectiveness of this depends on the

- 2 -

presence of a cobalt salt catalyst, moreover the speed of
oxygen removal is limited by the oxygen permeability of
the polyester. Further methods include sandwiching
crystalline oxidisable material between the layers of
5   multilayer containers, and including a catalyst for th
reaction of oxygen with hydrogen in a sandwich arrangement
as above or as a deposit on the inner surface of the
package.

Heterogeneous systems such as described above do not,
10   however, adequately meet the general needs of the
packaging industry, largely because they are often
oxygen-sensitive prior to use or can be activated only
under restricted conditions of, for example, temperature
or humidity. US Patent No. 5211875 proposes a composition
15   intended to avoid the problem of oxygen-sensitivity prior
to use, involving an oxidizable organic compound
(typically 1, 2-polybutadiene)and a transition metal
catalyst (typically cobalt salt). Oxygen scavenging is
initiated by exposing the composition to an electron beam,
20   or ultraviolet or visible light.

However, the inclusion of a transition metal catalyst
has a number of disadvantages including added cost,
solubility difficulties, and a "gritty" appearance and
reduced transparency of films made from such
25   compositions. Some transition metal catalysts are also
considered toxic and may not, therefore, be used with food.

The present invention avoids the disadvantages of
including a transition metal catalyst. It may be based on
plastic or other polymer-based compositions which can be
30   activated as required, to effect reduction of ambient
oxygen levels.

Accordingly, in a first aspect the present invention
provides a composition for reducing the concentration of
molecular oxygen present in an atmosphere or liquid,
35   comprising at least one reducible organic compound which

is reduced under predetermined conditions, the reduced
form of the compound being oxidizable by molecular oxygen,
wherein the reduction and/or subsequent oxidation of the
organic compound occurs independent of the presence of a
5   transition metal catalyst.

     Preferably, the reduction and/or subsequent oxidation
of the at least one reducible organic component is also
independent of the presence of an alkali or acid catalyst.

     The reducible organic compound for use in this
10   invention may be reduced under predetermined conditions
such as by exposure to light of a certain intensity or
wavelength or, alternatively, by the application of heat,
γ-irradiation, corona discharge or an electron beam.
Possibly, also, the compound may be reduced by
15   incorporating in the composition a reducing agent which in
turn can be activated under predetermined conditions, say
by heating.

     Typically the reducible organic compound will be a
compound having the capacity to be converted to an excited
20   state such as a triplet form, which then becomes reduced
to an essentially stable state by gaining or abstracting
an electron or hydrogen atom from other molecules or by
redistributing an electron or hydrogen atom within the
compound itself. The reduced molecule is reactive towards
25   molecular oxygen to produce activated species such as
hydrogen peroxide, hydroperoxy radical or a superoxide
ion. Preferably, the reducible organic compound is stable
in air at room temperature or is in its fully oxidized
state. Examples of suitable compounds include quinones,
30   such as benzoquinone, anthraquinone (preferably,
9,10-anthraquinone) and naphthoquinone (preferably,
1,4-napthoquinone); and photoreducible dyes and carbonyl
compounds which have absorbance in the UV spectrum, such
as azo, thiazine, indigoid and triarylmethane compounds.
35   Most preferably, the reducible organic compound is a

- 4 -

substituted anthraquinone such as 2-methylanthraquinone
and 2-ethylanthraquinone. In some applications,
2-ethylanthraquinone shall be preferred to
2-methylanthraquinone due to its greater solubility.

5   The reducible organic compound component may comprise
0.1-99.9 wt% of the composition. More preferably, the
reducible organic compound comprises 0.1-50 wt% of the
composition.

           Compositions of this invention which involve the
10   formation of an activated oxygen species (eg, peroxide)
may further comprise a scavenging component reactive
towards the activated species. This may be embodied in
the reducible organic compound itself, for example a
quinone having an amine group would be effective, but in
15   any event it should be an agent which is substantially
stable in contact with air at room temperature. Suitable
examples of the activated oxygen scavenging component
include antioxidants such as alkylated phenols and
bisphenols, alkylidene bis-, tris- and polyphenols, thio-
20   and bis-, tris- and polyalkylated phenols, phenol
condensation products, amines, sulfur-containing esters,
organic phosphines, organic phosphites, organic
phosphates, hydroquinone and substituted hydroquinones;
inorganic compounds such as sulphates, sulfites,
25   phosphites and nitrites of metals, particularly those of
groups 1 and 2 of the periodic table and first row
transition metals, zinc and tin; sulfur-containing
compounds such as thiodipropionic acid and its esters and
salts, thio-bis(ethylene glycol β-aminocrotonate), as
30   well as the amino acids cysteine, cystine and methionine;
and nitrogen-containing compounds capable of reacting with
activated forms of oxygen include primary, secondary and
tertiary amines and their derivatives including polymers.
           Preferably, the scavenging component reactive towards
35   the activated oxygen species is selected from the group
consisting of triphenylphosphine, triethylphosphite,

triisoproppylphosphite, triphenylphosphite,
tris(nonylphenyl) phosphite, tris(mixed mono- and
bis-nonylphenyl) phosphite, butylated hydroxytoluene,
butylated hydroxyanisole, tris(2,4-di-tert-butylphenyl)
5   phosphite, dilaurylthiodiprpionate,
2,2'-methylene-bis-(6-t-butyl-p-cresol),
tetrakis(2,4-d-tert-butylphenyl)4,4'-biphenylene
diphosphonite, poly(4-vinylpyridine) and mixtures thereof.
        The activated oxygen species-scavenging component may
10 be in the form of a polymer or oligomer. Such forms may
be prepared by, for example, covalently bonding a compound
such as those activated oxygen species-scavenging
compounds listed above to a monomer or co-monomer.
A limitation on the molecular size of the activated oxygen
15 species-scavenging component will be the effect, if any,
it has on functional properties of any other polymer with
which it is combined as in blending for instance.
        The activated oxygen species-scavenging component may
comprise 0.1 to 99.9 wt%, more preferably, 0.1 to 50 wt%
20 of the composition.
        As an alternative to components which can be excited
to a state which converts oxygen to an activated species,
compositions according to this invention may comprise
components which are excitable to a state in which they
25 react and bind directly with oxygen diffusing into the
composition from the surroundings.
        The compositions according to the invention may
further comprise an adhesive (eg, a polyurethane such as
LAMAL) and/or a polymer. Preferred polymers are
30 homogenous and include polyvinyls, polyolefins and
polyesters or their copolymers, ethyl cellulose and
cellulose acetate. Heterogeneous substrates, eg inorganic
polymers such as silica gel or polymer mixtures may also
be used.
35   Alternatively or additionally, the reducible organic

- 6 -

compound itself maybe in a polymerised form either as
homopolymers or copolymers. Oligomer forms may also be
suitable. Reducible monomers can be made by covalently
bonding an ethylenically unsaturated group to a reducible
5   organic compound. The reducible organic compound may also
carry groups capable of reaction with other polymerisable
molecules and preformed polymers. Particular examples of
ethylenically unsaturated reducible monomers include vinyl
and isopropenyl derivatives, preferably bonded to the
10   reducible organic compound in such a manner as not to
decrease the lifetime of the triplet excited state
compared with that of the unsubstituted reducible organic
compound. Thus in the case of 9,10-anthraquinone
substitution occurs preferably at the 2, 3, 6 or 7
15   positions. If such a reducible organic compound carries
additionally further substituents besides the vinyl or
isopropenyl group, such substituent should preferably be
in one or more of the remaining preferred positions.
     Co-monomers can be any ethylenically unsaturated
20   substance whether mono-unsaturated, di-unsaturated or
polyunsaturated. Examples include alkenes of carbon
number two to eight, vinyl acetate, vinyl alcohol, acrylic
monomers including methacrylic and acrylic acids, their
amides, esters and metal salts as in ionomers,
25   acrylonitrile, methacrylonitrile, norbornene,
norbornadiene. If the reducible organic compound is a
substituted 9,10-anthraquinone and is required to be
difunctional monomer for formation of a polyester, the two
carboxyl or hydroxyl substituents, or their derivatives
30   should preferably be in any two of the positions, 2, 3, 6
or 7.
     Reducible monomers may be polymerised as condensation
polymers such as polyesters, including polycarbonates,
polyamides, polyimides. An example of a polyamide is the
35   polymer of 2,6-anthra-9,10-quinone dicarboxylic acid with

1,6-diaminohexane. Reducible monomers may also be
polymerised with diisocyanates or diols to form
polyurethanes or may be bonded to polyurethanes. An
example of the latter is the reaction product of
5 2-bromomethyl-9,10-anthraquinone with the polyurethane
from toluenediisocyanate and 1,6-hexandiol.
      Preferably, the composition according to the
invention comprises a reducible organic compound and an
activated oxygen species-scavenging form, both of which
10 are present in polymerised form(s).
      Where the reducible organic compound is dispersed or
dissolved in a polymer which does not readily donate a
hydrogen atom or electron to the reducible organic
compound in its excited state, an additional source of
15 labile hydrogen or electron is preferred. Such a compound
is preferably one containing a hydrogen bonded to
nitrogen, sulfur, phosphorus or oxygen especially where a
hydrogen is bonded to a carbon atom bonded to the
abovementioned heteroatom. Alternative sources of
20 electrons are salts of organic compounds such as the salts
of sulfonic acids or carboxylic acids. In one form of the
invention the sodium sulfonate salt of a polymerised
9,10-anthraquinone would be used. Thus the reducible
organic compund itself can be the source of its own
25 electron for the reduction process.
      The reduced form of the organic compound used in the
composition, brings about a reduction in the molecular
oxygen concentration in the atmosphere or liquid through
its oxidation by the molecular oxygen, the reduction
30 and/or oxidation being independent of the presence of a
transition metal catalyst and, preferably, also
independent of the presence of an alkali or acid
catalyst. Nevertheless, transition metal compounds,
alkaline and/or acidic agents may also be included in the
35 compositions where they may effect the rate of oxygen

scavenging or may enhance the reduction and/or subsequent
oxidation of the organic compound. For example, ascorbic
acid may be included in the compositions comprising
anthraquinones as a photoreduction enhancer.

5   Reduction of the reducible organic compound may take
place only when convenient. This might be, for example,
when the composition is being made into or brought into
association with packaging material or, alternatively and
perhaps more usually, after formation of a package and
10   prior to filling and sealing. Reduction may even be
deferred until after sealing of the package.

        Thus, in a second aspect, the invention provides a
method for reducing the concentration of molecular oxygen
present in an atmosphere or liquid, comprising exposing
15   the atmosphere or liquid to a composition according to th
first aspect and thereafter, reducing the reducible
organic compound.

        Alternatively, the invention provides a method for
reducing the concentration of molecular oxygen present in
20   an atmosphere or liquid, comprising exposing the
atmosphere or liquid to a pre-reduced form of a
composition according to the first aspect.

        The compositions according to the invention may be
used independently or as components of blends. They may
25   take the form of a cross-linked polymeric matrix, as in a
can lacquer, or be bonded to or absorbed onto an inorganic
polymer, such as silica. They may be effectively applied
as, or incorporated in, for example, bottle closure
liners, PET bottles, liners for wine casks, inks,
30   coatings, adhesives, films or sheets either alone or as
laminations or co-extrusions, or they may take the form of
pads, spots, patches, sachets, cards, powders or granules
which may be attached to packaging material or located
independently within a package.

35   Films comprising the composition according to the

invention may be monolayer or multilayer laminate, and may
be used on their own or may be affixed or applied to a
solid substrate (eg, a solid packaging material). Where
the film is a multilayer film, it is preferable that an
5   outer layer is an oxygen barrier film, so that the film
may be used in a manner such that only the layer(s)
containing the reducible organic compound is exposed to
molecular oxygen from the atmosphere or liquid for which a
reduction in molecular oxygen concentration is required.
10   Films comprising the composition may also be used is
as a chemical barrier to oxygen transmission through a
packaging material. Thus if a packaging material has a
certain oxygen permeability, the oxygen passing through it
from the outside environment into a reduced oxygen content
15   atmosphere within the package can be scavenged by the
reducible organic compound. The composition can be
dissolved or dispersed within the packaging material or
can be placed adjacent to it as an additional layer on the
inner side of the package.
20   In multilayer laminate films, an activated oxygen
species-scavenging component may be provided in a seperate
layer from the layer comprising the activatable component.
Film layers containing a reducible organic compound
may be formed either from molten plastic compositions
25   extruded to give a particular shape or dimensions or from
a liquid state which gives the final solid layer by
reaction, or evaporation of a volatile liquid. Plastic
compositions will often be extruded at temperatures
between 50°C and 350°C depending upon chemical
30   composition and molecular weight distribution. Extrusion
may be via a die to give a film layer either alone or as a
component layer of a multilayer coextrusion. The layer
comprising the reducible organic compound may be extruded
onto another substrate as in extrusion coating and
35   lamination. Extrusion may be followed by moulding as in
injection or blow moulding.

These processes can involve the formation of foams in some instances.

The composition according to the invention may also take the form of a printing ink, coating or lacquer.

5   These may or may not be pigmented. The printing inks, coatings and lacquers will normally be applied in a liquid state and solidified by evaporation of the solvent or dispersion medium or by reaction of some. of the constituents.

10   While the composition and methods according to the invention are likely to be of particular value in food-packaging situations where oxygen removal is desirable, their utility is not limited thereto. Other applications include, for example, the generation of

15   low-oxygen atmospheres in vessels for anaerobic or microaerophilic microbiology, or the generation of low-oxygen gas for blanketing flammable or oxygen-sensitive materials.   The technology can also be used in conjunction with technologies based on other means

20   of oxygen scavenging such as photosensitized generation of carbon dioxide.

Compositions according to the invention may be re-reduced, if necessary, by resubjecting to the predetermined condition to recommence oxygen scavenging.

25   This may be particularly useful if the composition has been exposed to air prior to package sealing. Re-reduction may be achieved at a light intensity as low as ambient room illumination for an hour depending upon the amount of re-reduction required.

30   In addition to the advantages disclosed above, the method can, in some instances, be practised with compositions formulated to be self-indicating in respect to their capacity for oxygen removal. That is, some reducible organic compounds upon reduction will undergo a

35   change in colour or change in UV-visible, infrared or

- 11 -

near-infrared absorption spectrum. For example,
photoreduction of quinones and some of their derivatives
results in a spectral shift from the UV to longer
wavelengths, especially to the visible region of the

5   spectrum; by incorporation of such compounds, package
material can be formulated which will undergo a colour
change as the capacity for reducing the oxygen
concentration becomes exhausted.

This colour change also provides a mechanism for
10 checking whether all of the reducible organic compound in
the composition has been reduced. Where reduction is
found to be incomplete, the composition may be resubjected
to the predetermined conditions. Further, such
compositions may also be used as an indicator of seal

15 breakage. That is, in the area of film where a heat seal
or other seal is made between the film containing the
reducible organic compound and a material of sufficiently
high oxygen barrier, oxygen cannot reach the reducible
organic compound as fast as it can in other areas. The

20 seal area therefore remains coloured due to the presence
of reduced organic compound. The fluorescent emission
from the reduced organic compound is particularly useful
for this purpose. A green fluorescence is seen when
9,10-anthraquinone with substitutents in the 2-position

25 are bonded by a methylene group to the ring.
Alternatively, a strip or ring of the composition may be
located on the inner side of the sealed package adjacent
to the seal. Where the seal is formed by an adhesive, the
composition may comprise the adhesive. If the seal should

30 be incomplete or become broken in any way, then this may
be detected by a colour change in the composition.

Visible colour changes may be detected by eye,
whereas changes in UV-visible, infrared or near infrared
absorption spectrum may be measured with an appropriate

35 device such as a photocell used with a light source of
appropriate wavelength and intensity.

- 12 -

The invention will now be further described with reference to the following non-limiting examples and figures.

Brief Description of the Figures

5   Fig. 1: Photoreduction of 2-methyl-9,10-anthraquinone (0.075M in ethyl cellulose, heat sealed between two layers of PVDC-coated polypropylene). Spectra show the photoreduction of the sample under xenon lamp irradiation (0, 30, 90, 180, 300 and 600 seconds) and detail the
10   decline of the peak at 327nm, with a corresponding increase in the peak at 375nm, as irradiation time increases.

Fig. 2: Photoreduction of 2-methyl-9,10-anthraquinone (0.075M in ethyl cellulose, heat sealed between EVOH
15   barrier laminate and SURLYN1601) under xenon lamp irradiation (0, 30, 90, 180, 300 and 600 seconds). The peak at 327nm decreased with increasing irradiation time, while the peak at 375nm increased until approx. 300s irradiation, when it began to decrease.

20   Fig. 3: Reoxidation of reduced species in air after storage for 106 days under nitrogen. The reoxidation involves the gradual loss of the peak at 375nm with a corresponding increase in the peak at 327nm. The three spectra shown above correspond to the film sample reduced,
25   and then after 1 day and 21 days left to oxidise.

Example 1. Photoreduction and reoxidation of anthraquinone in ethyl cellulose.

9,10-Anthraquinone, 0.05g, and ethyl cellulose (degree of substitution, 2.5), 1.5g, were dissolved in
30   ethyl acetate, 12ml. The solution was cast onto plastic coated glass to give a film 10-15μ thick when the solvent had evaporated. A sample of the film was placed in a nitrogen flushed spectrophotometric cuvette and the absorbance at 252.nm and 264.nm was measured.

35   While still in the cuvette under nitrogen, the sample

- 13 -

was irradiated for 20 seconds with light from a xenon lamp
using a Suntest CPS instrument, and the ratio of
absorbance at 254.8 to that at 264.3 measured. The sample
was exposed to air for a total of 10 days to allow

5 reoxidation of the anthrahydroquinone and/or the
semi-quinone, which would result in the absorbance ratio
returning towards its initial value. The results in Table
1 show that photoreduction occurs on irradiation, followed
by reoxidation upon exposure to air. Slight shifts in

10 A_{max} occurred with reduction and oxidation.

Table 1.

Treatment	Absorbance Ratio		
	254.3/264.3	252.4/264.3	252.8/264.3
None	2.10		
Irradiated (20s)		0.93	
3 days in air			1.44
6 days in air			1.49
10 days in air			1.50

15 is column heading marker; 20 marks the "Irradiated (20s)" row; 25 marks Example 2.

25 <u>Example 2. Photoreduction of 2-methylanthraquinone in ethyl
cellulose sandwiched between two layers of polyvinylidine
chloride copolymer-coated polypropylene</u>

2-methyl- 9,10-anthraquinone (hereinafter referred to
2-methylanthraquinone or MeAq), 0.0167g, was dissolved in

30 ethyl acetate, 9ml, together with ethyl cellulose, 1.15g,
and a film was cast as in Example 1. The film was 20-30 μm
thick. A strip of this film was placed between two layers
of the PVDC-coated polypropylene, and the two outer layers
were heat sealed together to form a flat package

35 containing the ethyl cellulose layer with essentially no
headspace.

The 3-layer sample was held in a steel clamp and

- 14 -

exposed for seven time intervals to the light from the xenon
lamp as in Example 1. The maximum exposure was 10 minutes
and the absorption spectrum was measured with a
spectrophotometer after each exposure. The results in

5   Figure 1 show the decrease in absorbance due to
2-methylanthraquinone at 327 nm with increase in absorbance
at 375 nm (and at longer wavelengths) due to progressive
formation of the corresponding anthrahydroquinone and/or
semiquinone.

10   These results indicate that a barrier plastic film
permits the photoreduction of the 2-methylanthraquinone
without the interference by atmospheric oxygen.
Example 3. Photoreduction of 2-methylanthraquinone in ethyl
cellulose sandwiched between a layer of Surlyn 1601 (Du

15   Pont, Wilmington, USA) and a co-extruded film of Surlyn,
ethylene vinyl alcohol copolymer and nylon 6
       A sample of the ethyl cellulose film described above in
Example 2 was placed between one high-permeability layer
(Surlyn 1601) and one low-permeability layer (the

20   co-extrusion) containing ethylene vinyl alcohol as barrier.
This would allow testing whether the low barrier is
sufficient to stop oxygen interference with the
photoreduction.
       The film sandwich was illuminated and the spectra were

25   measured as in Example 2. The spectra in Figure 2 show that
the quinone is photoreduced but with some decrease in
efficiency compared with the previous Example and with some
evidence of side reaction. This result indicates that the
oxygen permeability of either the layer provided by the

30   Surlyn or the layer containing the quinone should preferably
be reduced.
Example 4. Scavenging oxygen from air in pouches made from
a high-oxygen-barrier plastic
       2-Methylanthraquinone, 0.05g, was dissolved in ethyl

35   acetate, 9ml, together with ethyl cellulose, 1.25g and a

WO 94/12590

film cast 19cm x 18cm on the Surlyn side of the co-extruded
film described in Example 3. This sample was termed the
"control" and was folded to form a pouch of dimensions 23cm
x 20cm. The pouch was flushed with nitrogen and exposed to
5   xenon lamp irradiation as per Example 3 for 3 minutes. Some
nitrogen was then removed by syringe via a septum and air,
20ml, was added and the oxygen content measured by gas
chromatography. (The quantity of 2-methylanthraquinone is
approximately equimolar with 4ml of oxygen.) The pouch was
10   then stored in darkness.

Three additional pouches were prepared in a similar
fashion but with the addition of triphenylphosphine to
scavenge the hydrogen peroxide or formed derivative. The
quantities of triphenylphosphine were 0.059g, 0.118g and
15   0.295g. These pouches were treated in the same manner as
the pouch from the "control".

The oxygen content of the hour pouches was determined
again after storage for 25.3 hours and the initial and final
results are shown in Table 2.

20   The film has an oxygen transmission rate of $6cc/m^2/$
day/atmosphere at $20^{\circ}C$ 75% RH.

Table 2. Oxygen scavenging in the presence of
triphenylphosphine

Triphenylphosphine (g)	Initial oxygen (%)	Oxygen After 25.3 hrs (%)	Final oxygen (%)
0	20.3	16.1	14.05
0.059	10.45	3.9	2.8
0.118	15	1.17	0.35
0.295	14.6	0.07	0.16

Preparation of the films was repeated with an
additional one containing triphenylphosphine at a level of
0.59g, as well as the 2-methylanthraquinone, but this time
the pouches were opened after irradiation and the ethyl

- 16 -

cellulose layers removed, placed in Quickfit test tubes and
stoppered. The test tubes were stored in darkness for 24
hours.

5   Potassium iodide, 1% w/w in water was prepared and 4ml
of this solution was added to each of the test tubes.
Freshly prepared starch mucilage, 2ml, was also added and
the test tubes were shaken vigorously for 30 seconds. The
test tubes were allowed to stand in darkness. After 5
minutes the test tube containing the "control" film
10   contained black stained film due to the release of iodine
formed through action of the hydrogen peroxide or its
derivative. The film containing triphenylphosphine, 0.059g,
showed a slight blue stain only after 3 days. The remaining
films showed no evidence of iodine formation indicating no
15   release of hydrogen peroxide from the films.

Example 5. Oxygen scavenging using a polymerised reducible
organic compound

2-Vinylanthraquinone, 0.25g, was dissolved in benzene,
30ml, and benzoyl peroxide, 0.01g, was added. The solution
20   was degassed by free-thaw evacuation and polymerisation was
carried out at reflux temperature for three hours during
which time a precipitate was formed. The solvent was
removed and the polyvinylanthraquinone was mixed with
triphenylphosphine, 0.059g, and octanol-1-ol, 5 drops, in
25   chloroform. The resulting solution was cast on the Surlyn
side of the co-extrusion described in Example 3, with an
area of approximately 25cm x 20cm. A pouch was formed by
heat-sealing this film to another piece of co-extrusion and
the air was removed by evacuation. Nitrogen was injected
30   into the pouch and this was irradiated as in Example 4.
Most of the nitrogen was removed and replaced with air,
20ml, as in Example 4.

The oxygen content of the pouch was found to be 17.4%.
The pouch was held in darkness and the oxygen content was
35   found to be 10.7% after 4 hours and 10.6% after 22.5 hours.

- 17 -

Example 6. Oxygen scavenging by 2-methylanthraquinone in a
UV-cured varnish

A mixture of a commercial UV-curable varnish, 50 parts,
and ethanol, 50 parts, was used to dissolve

5   2-methylanthraquinone as a 5% solution. This mixture was
applied to a polypropylene film as a 2 to 3 μm thick layer
using a pilot scale coating machine. Strips of the coated
polypropylene approximately 20cm x 20cm, were cut and placed
in pouches made from the film described in

10   Example 4. After nitrogen flushing the pouches were exposed
to xenon lamp irradiation for periods of time shown in
Table 3. The nitrogen was removed and 200-250ml of nitrogen
containing 0.5% oxygen was injected into each pouch. The
scavenging of oxygen was determined by gas chromatography

15   and the volume of oxygen consumed after 1 hour is shown in
Table 3.

Table 3. Oxygen scavenging by a UV-cured varnish
containing 2-methylanthraquinone

Irradiation Time (sec)	% of total oxygen scavenged after 1 hour
1	50
2	28
3	3
4	31
5	27
6	19

Similar results were obtained when ethyl cellulose was
used instead of the UV-curable varnish.

Example 7. Oxygen scavenging in the presence of carbon
dioxide

35   Two pouches were prepared as described in Example 4
with triphenylphosphine and 2-methylanthraquinone contents
of 0.118g and 0.055g respectively in the ethyl cellulose
layer, 1.25g. After nitrogen flushing and irradiation as
per Example 4 the pouches were evacuated and filled with

- 18 -

20ml each of air and carbon dioxide. The pouches were
stored in darkness and the oxygen concentration was
monitored by gas chromatography.

The results are shown in Table 4 and comparison with
5   the result for the corresponding pouch without carbon
dioxide after 25.3 hours storage (Table 2) shows very little
difference in scavenging rate. Current scavengers based on
iron powder are often inactivated or have their scavenging
rate severely retarded by the presence of carton dioxide.

10 **Table 4**

Time(h)	Oxygen Concentration (%)	
	Pouch 1	Pouch 2
0	8.3	7.8
5.5	6.2	6.3
22.0	3.3	3.4
46.0	1.9	1.4

Example 8. Stability of Scavenging Capability
The reactivity towards oxygen of the photoreduced
2-methylanthraquinone in ethyl cellulose after 106 days
storage in the absence of oxygen was demonstrated as
25 follows. Ethyl cellulose, 1g and 2-methylanthraquinone,
0.018g, were dissolved in ethyl acetate, 9ml, and cast as
five films measuring approximately 10cm x 10cm x 2q0μm on
the surface of the co-extruded barrier film based on
ethylene vinyl alcohol described in Example 3.

30   One of these coated films was made into a pouch and
the air was removed and replaced by nitrogen. The film
was irradiated as in Example 4 and the pouch was stored in
an atmosphere of nitrogen for 106 days. The UV-visible
spectrum was measured after which the pouch was opened to
35 allow air to replace the nitrogen in the pouch. The
spectrum was measured after one day and 3 weeks.

The spectra are shown in Figure 3 which shows that
the reduced species reoxidises with a decrease in
absorbance at wavelengths above 350nm and and increase

- 19 -

around 330nm characteristic of the reoxidation of the
anthrahydroquinone or semiquinone species to the quinone
form.

Example 9.   Photoreduction and reoxidation of
2-methylanthraquinone in the presence of
poly(4-vinylpyridine)

    A solution of 2-methylanthraquinone and ethyl
cellulose in ethyl acetate was prepared and cast into
2 separate films as in Example 4. One of the films was
coated over part of its area with a film of
poly(4-vinylpyridine), PVP, made by casting a solution of
0.7g of polymer from methanol solution followed by solvent
evaporation.

    The film samples were formed into pouches and
irradiated using the techniques described in Example 4.
After irradiation the pouches were opened and the excess
co-extruded barrier packaging material was cut off. The
samples were placed with the ethyl cellulose-coated side
uppermost in plastic dishes where they were left in air
for 4 days.

    The samples were then covered with the
starch/potassium iodide solution described in Example 4.
The solution covering the sample not coated with PVP
turned dark blue/black within a few minutes. The solution
covering the PVP-coated area of the second sample did not
become coloured even after several hours whereas the
solution covering the uncoated areas coloured the same as
was found with the uncoated sample.

    The results indicate that the PVP scavenged the
oxidizing species such as hydrogen peroxide formed in
reoxidation of the photoreduced 2-methylanthraquinone.

Example 10. Oxygen scavenging in the cold

    A pouch was made from film comprising
2-methylanthraquinone, 0.055g, with ethyl cellulose, 1.25g
and triphenylphosphine 0.118g as described in Example 4.

20ml of air was added and the pouch stored at -1.0 to 1.0°C.

Results :	Time (days)	% oxygen
	0.0	19.6
	1.	8.04
	2.	6.22
	3.	4.49
	6.	3.03
	13.	1.64
	17.	1.21
	41.	1.13

Example 11. <u>Dependence of scavenging upon irradiation time and delay between irradiation and exposure to air</u>

Ethyl cellulose, 1.2g, and 2-methylanthraquinone, 0.118g, were dissolved in ethyl acetate, 9ml, and cast as four films onto the Surlyn side of CSDE film and made into pouches with the test film folded over onto itself and a half slice of tissue inserted between. All were vacuum packed in the Turbovac, then two were given a total of five minutes irradiation (half each side) and the other two ten minutes. One each of the pouches immediately had 20ml of air injected, the other two being left overnight before they too had 20ml of air introduced. This tested for whether leaving the films after reduction has any effect on their oxygen scavenging.

Results :

	Filled immediately		Left overnight	
Time (h)	5M	10M	5M	10M
0.0	21.	21.	21.	21.
2.	6.49	5.91		
4.5			6.35	6.32
19.5	0.57	0.3		
21.8			0.75	0.29
24.	0.23	0.28		
28.8			0.27	
50.	0.2			

The results show that irradiation time may have some effect on rate of scavenging, but it is small between 5 and 10 minutes. Also, leaving the pouches prior to

- 21 -

filling seems to have no effect.

Example 12. Peroxide scavenging from a separate film

Films Cast:	MeAq (g)	NQ (g)	TPP (g)	EthCell (g)
	0.055	---	---	1.2
	---	0.039	---	1.2
	---	---	0.118	1.2

The 2-methylanthraquinone and 1,4-naphthoquinone (NQ) films were cast directly onto CSDE, with the triphenylphosphine (TPP) films cast onto polethylene cling wrap, then placed on top of the others, flattened out, and the edges taped down. Holes were punched through the TPP film so that it would not blow up when placed in the Turbovac. Bags were vacuum packaged and given 10 minutes irradiation before having 20ml of air injected.

Results

		% oxygen	
Time (h)		MeAq	NQ
0.0		21.	21.
2.		14.45	
4.8			17.75
18.8		5.03	
23.3			12.
25.8		4.47	
44.3		1.89	
89.		.	2.86
114.8		0.61	
166.3			1.28
187.3		0.81	

Example 13. Photoreduction on the coater-laminator

Films cast:	MeAq (g)	TPP (g)	EthCell(g)
	0.055	0.118	1.2
	---	0.12	1.2 (onto polyethylene cling film)
	0.055	---	1.2

Pouches were set up in a similar way to previous examples, but irradiation was with a coater-laminator at a web speed of 5m/min. The UV lamps cast a beam of light approximately 10cm long, and thus the samples were

- 22 -

irradiated for an average of 1.2 seconds. As in previous tests, 20ml of air was injected.

Results:

Time (h)	Type a	Type b	Type c	Type d
		% oxygen		
0.0	21.	21.	21.	21.
2.			13.47	17.87
4.5			12.91	16.12
5.3	5.95	2.05		
7.	2.35	0.36	11.53	15.77
24.	0.17			
77.			2.18	10.89

(a) and (b)-MeAq and TPP in the one film.

(c) and (d)-TPP was in ethyle cellulose cast on polyethylene cling film.

The results appear to show that the scavenging performance is unaffected by the different method of photoreduction, and this was supported by the intense fluorescent colour of the film straight off the coater.

Example 14. Stoichiometry of the MeAQ reoxidation

Films cast:	MeAq (g)	TPP (g)	EthCell(g)
	0.055	0.118	1.2

Film was set up in a similar manner to previous examples, and irradiated for 10 minutes with the Xenon lamp before injecting 60ml of air (ie, oxygen:MeAq ratio of 3:1).

Results:

Time (h)	% oxygen
0.0	21.
89.5	9.52
115.	9.36

This result indicates a scavenging ratio of 1.7 moles of oxygen scavenged per mole of MeAq. Extraction and HPLC/V-VIS revealed that no TPP was present (2:1 molar ratio with MeAq) and this may be confirmation that more than a 1:1 molar amount of peroxide was produced by the MeAq reoxidation.

- 23 -

Example 15. Ferrous sulphate as a peroxide scavenger

Films cast: MeAq (g)   F.Sul(g)   EthCell(g)

5   0.055   0.344   1.2

      Pouches were prepared in a similar manner to the
previous examples with the ferrous sulphate heptahydrate
(F.Sul) (ground into fine powder) dispersed through it.
10 The pouch vacuum packed, and irradiated for 10 minutes in
the Xenon lamp, before 20ml of air was injected.
      0.0   21.
            2.3   16.27
            18.8   7.42
15   25.5   5.46
            114.8   2.53
            142.8   2.07
            190.8   1.6
            260.8   3.17
20   The results suggest that oxygen scavenging is slower
than when TPP is used

Example 16. Anthraquinone-2-aldehyde (AQ2A): inbuilt
peroxide scavenging

Films cast: AQ2A (g)   TPP (g)   EthCell(g)
25
                0.058   ---   1.2
                0.058   0.118   1.2

      Two films each were cast with the above quantities
and vacuum packed before being irradiated for 10 minutes
30 with the Xenon lamp and injected with 20ml of air.

Results:

        Time (h)   AQ2A1   Time (h)   +TPP1
        0.0   21.   0.0   21.
35   2.3   17.02   2.   8.61

- 24 -

Time (h)	AQ2A1	Time (h)	+TPP1
19.3	15.	4.	5.33
44.8	14.52	75.5	0.62
121.5	12.44		

Example 17. PEF as peroxide scavenger

Films cast:	MeAq (g)	PEF (g)	EthCell(g)
	0.055	0.072	1.2

Two pouches were made, the bis(furfurylidene) penta-erythritol (PEF) being 1:1 w.r.t. MeAq, vacuum packed, irradiated for 10 minutes with the Xenon lamp, and injected with 20ml of air.

Results:

Time (h)	MP1	MP2
0.0	21.	21.
4.	15.91	15.32
23.3	10.84	12.94
69.	7.38	12.78
148.5	2.29	1.82

Example 18.   Cellulose acetate as scavenging medium

Films cast:	MeAq (g)	TPP (g)	Cel.Ac.(g)
	0.1	0.1	1:4

The pouches were prepared in a similar manner to previous examples and were irradiated with the Xenon lamp.

Results:

Time (h)	CA1	CA2
0.0	21.	21.
5.3	19.2	8.57
Time (h)	CA1	CA2

- 25 -

Time (h)	CA1	CA2
23.5	1.3	1.05
30.3	5.14	0.38

Example 19. LAMAL Adhesive - TPP peroxide scavenging

Films cast:	EtAq (g)	L-HSA (g)	L-C (g)	EtOH (g)	TPP (g)
	0.1	1.8	0.2	3.	0.24

EtAq   = 2-ethyl-9,10-anthraquinone
L-HSA   = polyurethane base polymer
L-C   = cross linking agent for the polyurethane
    Films were cast onto warm plate (covered with polyester/polyethylene laminate) using the TLC spreader with a gap of 300μ. The adhesive was then laminated with PVC cling-wrap, and injected with 20ml of air.

Results:

Time (h)	Lamal 1
0.0	21.
1.5	12.01
18.5	0.62
22.3	0.47

    The results indicate that the films work well, although perhaps a little slower than TPP in ethyl cellulose.

Example 20. LAMAL - Triisopropyl phosphite (TIP) peroxide scavenging

Films cast:	EtAq (g)	L-HSA (g)	L-C (g)	EtOH (g)	TIP (g)
	0.1	1.8	0.2	3.	0.2

Two samples were pr pared as in Example 19.

- 26 -

Results:

Time (h)	Lamal2	Lamal3
0.0	21.	21.
3.	13.86	17.42
21.5	9.63	7.23
45.	4.19	5.36
189.	3.61	4.26

Example 21.   Triisopropyl phosphite peroxide scavenging from ethyl cellulose

Films Cast:	EtAq (g)	TIP (g)	EthCel (g)
	0.1	0.1	1.2

Film was cast onto EVOH barrier material using the TLC spreader with a gap of approximately 400 μ vacuum packed and irradiated as in previous examples.

Results:

Time (h)	TIP1	TIP2
0.0	21.	21.
2.3	19.46	12.01
22.2	7.14	5.58
96.3	4.03	0.36
452.	0.24	0.18

Example 22.   Use of gamma-irradiation for activation of ethyl cellulose films

A cobalt-60 source was used to provide a dose of 25 kilogray to films containing ethylanthraquinone and triphenylphosphite. The films were made as described below and the results provided in Table 5.

Ethylanthraquinone, 0.13 g, triphenylphosphite, 0.385g, and ethyl cellulose, 3.3 g, were dissolved in ethyl acetate and the resulting solution was spread on two sheets of poly(ethylene-terephthalate); 12 μm thick with the aid of a doctor blade. The solvent was evaporated by warming to approximately $40^{\circ}C$ for 10 minutes in a fume hood. The resulting plastic films had an area of 18cm x 22cm and was on average μm thick.

- 27 -

The films prepared as above were placed in pairs in the bags and either smoothed manually before sealing or were sealed under vacuum followed by addition of a known volume of air or nitrogen. The bags were made either from
5 metallised polyester laminated to polyethylene or were bag-in-box liners which contained an inner duplex liner of polyethylene as well as a sealed value socket. The area of each side of all bags was 18cm x 22cm.

The volume of air initially in each bag was between
10 200ml and 300ml. It can be seen that the film consumed oxygen highly efficiently.

Example 23. Use of gamma-irradiation for activation of ethylene vinyl acetate (EVA) films.

The irradiation treatments and the bags were the same
15 as in Example 22. The EVA films were cast from toluene solutions containing the compositions shown below. The EVA was obtained as a gel (Morton Chemical Co., USA) under the trade name Adcote 1133.

The Cetyl alcohol was used as the photoreducing agent
20 supplying labile hydrogen or electrons, a function which appears to be served by the polymer itself in the case of the ethyl cellulose, cellulose acetate, and polyurethan adhesive (Lamal).

Cetyl alcohol, 0.32g, triphenyl phosphite, 0.68g, and
25 2-ethylanthraquinone, 0.4g, were dissolved in the toluene gel of EVA, 12.5g, to give a mobile solution. This was then cast into a film layer on the heat seal side of a 2 sheets of oxygen barrier plastic of ionomer/EVOH/polyester of oxygen transmission rate/cm^3/m^2/24 hr/atmosphere at
30 $25^{\circ}C$, 75% RH. The area of film and thickness were as in Example 22.

The scavenging of oxygen present either prior to irradiation or injected into the bag after irradiation is shown in Table 6.

Table 5.

Bag	Oxygen % Initial	Final[1]	Activatable Component
PET/Pe	20.6	9.0	2-EtAQ[2]
PET/Pe	20.6	8.3	2-EtAQ
Bag-in-Box	20.6	2.8	2-EtAQ
Bag-in-Box	20.6	5.6	2-EtAQ

1.   3 days after γ-irradiation

2.   2-ethylanthraquinone

Table 6.

Bag	Oxygen % Initial	Final[1]	Activatable Component
Bag-in-Box	20.6[3]	14.1	2-EtAQ[2]
Bag-in-Box	20.6[3]	10.8	2-EtAQ[2]

1,2   as per Table 5

3   air injected 24 hours after irradiation.

<u>Example 24.   Activation with Electron Beam</u>

Films Cast:

Sample	EtAq(g)	TPP	TIP	EthCell(g)
A	0.06	0.12		1.2
B	0.06		0.14	1.2

Pouches were prepared in a similar manner to previous examples. The total volume of the bags was measured, and this value was used to calculate the volume of oxygen (from air) initially present. Oxygen analysis was carried

out 23 hours after the pouches were made, and the volume
of oxygen scavenged calculated. This was then converted
into the percentage of the stoichiometric amount scavenged
(% Stoich.), which compares the actual volume of oxygen
5   scavenged with the theoretical maximum which could be
scavenged (assuming a 1:1 interaction of oxygen with
anthraquinone).

Results:
10 Sample   Dose Rate (MRads)   % of Stoich

Sample	Dose Rate (MRads)	% of Stoich
A	3.0	68
B	1.1	32
C	3.0	80

15   The results show that the electron beam is an
efficient method of inducing photoreduction and bringing
about oxygen scavenging, even at lower dose rates.

Example 25. Oxygen scavenging from a tinplate can

        A crosslinkable polyurethane resin was used to
20 demonstrate the use of an oxygen-scavenging coating on the
inside of a tinplate can.

        A can of volume 465 ml was coated internally with a
solution of Lamal HSA, 3.64g, and Larmal C, o.54g,
2-ethylanthraquinone, 0.33g, and triphenylphosphite,
25 0.33g, in ethanol 6g. The solvents were evaporated at
50-60°C leaving a coating of polyurethane resin
containing 2-ethylanthraquinone and triphenylphosphite on
the inside of the can. The can was then exposed to
irradiation in the solar simulator for five minutes and
30 then filled loosely with glass beads to reduce the
headspace to 170ml and the can was then sealed by
double-seaming.

        The headspace gas was anaylsed after 24 hours by
which time the oxygen concentration had been reduced from
35 20.6% to 19.5%. The oxygen consumed was 2.5ml. This

- 30 -

represents the quantity of oxygen which can be found
sometimes in commercial cans.

Example 26. Oxygen Scavenging with a Copolymerised
Reducible Organic Compound

5   Copolymers of 2-vinylanthraquinone were made with
styrene (STY) and with 2-hydroxyethyl methacrylate
(HEMA). The copolymers contained approximately 9 moles %
of polymerised anthraquinonoid monomer.

         Films were cast on the Polyester/EVOH/Surlyn barrier
10   film as described in other examples using the quantities
shown below. The HEMA copolymer and its blend from ethyl
cellulose were cast from ethanol and the styrene copolymer
was cast from a mixture of chloroform (70%) and acetone
(30%). The films were made into pouches and the air was
15   removed as in other examples. The pouches were irradiated
for 5 minutes on each side in the Suntester solar
simulator and 20ml of air was injected into each pouch,
except for that containing the blend which was injected
with 50ml of a mixture of 2.1% oxygen in nitrogen.
20

Quantities of Ingredients (g)

Test	HEMA Copolymer	STY Copolymer	$C_6H_5O)_3P$	Cetyl Alcohol	Ethyl Cellulose
A	0.6	-	0.11	-	-
B	0.25	-	0.10	-	1.0
C	-	0.5	0.11	0.09	-

- 31 -

Results:

<u>% Oxygen</u>

Time (h)	Test A	Test B	Test C
0	21.0	2.1	21.0
17.0	–	1.2	–
64.7	15.4	–	16.0

The results show that the polymers scavenge oxygen, but their permeability to oxygen can result in slower scavenging than with a highly permeable film such as ethyl cellulose.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.